

EQUATION OF STATE
AND
HEAT CONTENT OF URANIUM

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1. General Method

This report presents some calculations made on the equation of state of uranium at high temperature and pressure. Included are estimates of internal energy, entropy and the adiabatic work available from varying high pressure states of several reduced pressures.

Experimental data for U exist only at temperatures slightly above the melting point (1630-1970°K), including particularly the experiments of Rauh and Thorn¹ which extend up to 1970°K. The temperatures of interest to us are 10 and more times higher. For such temperatures, one must rely upon estimates based on "universal" relations among various thermodynamic variables. These relations employ the principle of corresponding states which says that all substances are equivalent at a given specification of corresponding or reduced variables. It is customary to reduce the variables by dividing them by their values at the critical point, this being the most obvious corresponding point. Thus our first task is the evaluation of the critical constants.

Estimates of the critical temperature and pressure on this basis have been made by Elrod². He finds

$$T_c = 14,200^\circ$$

$$P_c = 5,130 \text{ atm.}$$

For most substances $(P_c V_c / RT_c) = 0.3$. With this value, the above figures yield $V_c = 68 \text{ cm}^3$ (V_c = molar volume at critical point). This value of V_c is extremely large in that for typical substances $V_c = 3.11 V_{\text{solid}}$ (Cf. Hirschfelder, et al³ p.238). For U in the solid state, $\rho = 19.1 \text{ g/cm}^3$ or $V_{\text{solid}} = 238/19.1 = 12.5 \text{ cm}^3$, thereby leading to $V_c = 39 \text{ cm}^3$. As the volume of the solid at low temperatures should be a reliable corresponding quantity we are inclined to keep V_c based on this estimate and to reject the estimate of 68 cm^3 . In order to maintain $P_c V_c / RT_c = 0.3$ which is usually a reliable constant, we must then reject at least one of Elrod's critical constants.

That Elrod's value of T_c is reliable seems quite convincing because there is striking agreement between "predicted" and observed values for a large variety of substance as Elrod has demonstrated. Moreover, Elrod's extrapolation to T_c can be done in two ways, viz. (1) his own way, namely extrapolating the experiments of Rauh and Thorn¹ to the boiling point by a well-established empirical relation, and then using his theory from there on up to T_c , and (2) using the theory all the way from the experimental region to the critical point. In the latter case, Elrod's $\chi(\rho)$ is assumed to be a linear function of $\log \rho$ in the region of the experiments which is reasonable; the result of this calculation is $T_c = 14,000^\circ$ in excellent agreement with Elrod's original estimate.

We are inclined to reject Elrod's estimate of P_c for the following reasons: (1) The agreement between observed and "predicted" values for other substances is far from impressive, often having deviation between 15 and 30%. Further, almost all these other estimates are made on the basis of experiments at reduced temperatures $T/T_c = T^* \approx 0.5$ whereas the experiments by Rauh and Thorn are in the range of $T^* \approx 0.1$. (2) The calculation of Elrod leads to $\log P_c$ so that errors are compounded exponentially. For example, if Elrod's function $\bar{Q}(T_r)$ is taken to be linear down to the experimental range of Rauh and Thorn, one is led to $P_c = 900 \text{ atm}$, which is absurd. This necessitates extrapolation of the experimental data up to regions where $\bar{Q}(T_r)$ is known. This extrapolation is possible in determining T_c , but probably leads to large errors in P_c .

We shall, therefore, retain Elrod's estimate of $T_c = 14,000^\circ$, take $V_c = 40 \text{ cm}^3$ as based on V_{solid} and determine P_c from $P_c V_c / RT_c \approx 0.3$. This leads to $P_c = 8,650 \text{ atm}$.

2. Relevant Conditions

The equation of state which we wish to derive is to be applied to the problem of certain hypothetical reactor accidents. In these accidents it is assumed⁴ that the uranium is not present in a solid lump but in many small pieces separated by void spaces. Then the uranium can expand into the volume which was originally void. The total volume available to the uranium is greater than that of the liquid at the melting point, but in the interesting situations, less than the critical volume. We shall carry out our calculations for specific volumes.

$$V^* = V/V_c = 0.8 \text{ (Case I) or } 0.6 \text{ (Case II)}$$

3. Equation of State Calculations

As the molten metal heats up it expands. Vapor is formed to the extent given by the vapor pressure at each temperature, and the vapor fills the void. Eventually, as the temperature increases further, expanding liquid will fill the void and the system becomes one phase. It is possible to estimate the temperature when this happens by using the empirical law of rectilinear diameters (cf. Guggenheim⁵ p. 141). By reference to the graph of Guggenheim, it is seen that for $V^* = 0.8$ one arrives at a single phase at $T^* = 0.99$, and for $V^* = 0.6$, there is a single phase at $T^* = 0.96$. ($T^* = T/T_c$.)

Above this temperature, as the gas heats up it builds up pressure. It is desired to know P^* as a function of T^* . In all probability, none of the common empirical equations of state are adequate. In this situation we were led to the use of the compilations of Hougen and Watson⁶ where values of (PV/RT) are plotted against P^* for different values of T^* . The graphs represent the mean values of data from CO_2 , N_2 , H_2 , NH_3 , methane, propane and pentane. A method of trial and error was used. For a given P^* , a T^* was guessed (PV/RT) was then obtained from the graphs and one calculated back T^* , etc. The results are given in Table I.

TABLE I

(PV/RT) and P^* as functions of T^*

<u>(a) $V^* = 0.80$</u>							
T^*	1.10	1.23	1.50	1.76	2.3	2.9	3.4
(PV/RT)	0.40	0.59	0.80	0.96	1.04	1.24	1.41
P^*	1.85	3.0	5.0	7.0	10.0	15.0	20.0
<u>(b) $V^* = 0.60$</u>							
T^*	1.05	1.11	1.21	1.33	1.6	1.9	2.4
(PV/RT)	0.35	0.48	0.75	0.95	1.12	1.42	1.50
P^*	2.0	3.0	5.0	7.0	10.0	15.0	20.0

In addition to the tables of Hougen and Watson, values of (PV/RT) for argon are known (cf. Hirschfelder³ p. 306). These are:

$T^* = 1.69$	$V^* = 0.77$	$(PV/RT) = 1.13$
2.16	0.77	1.36
2.62	0.77	1.50
$T^* = 1.69$	$V^* = 0.64$	$(PV/RT) = 1.38$
2.16	0.64	1.64
2.62	0.64	1.80

The agreement is not very good, indicating that the attractive part of the potential in the data of Hougen and Watson is more dominant than in the case of inert gases. In view of our ignorance of the intermolecular potential, we shall work with the data of Hougen and Watson which cover a broad range of substances,

4. Calculations of Excess Energy

We term excess energy E^0 , the energy of the substance in excess of its energy as calculated for an ideal gas under the same thermodynamic conditions. It is a negative quantity resulting from cohesive forces among the atoms. From the data of Rauh and Thorn¹, the heat of vaporization is 106 kcals near the melting point. Thus for the stable liquid

$$(E^0/RT_c) = -3.8 \text{ with } T_c = 14,000^\circ$$

To get E^0 above $T^* = 1$, we again refer to the tables of Hougen and Watson. Here $(-H^0/T_c)$ is plotted against P^* for various T^* where H^0 is the excess enthalpy. To convert to energy we note that

$$H = E + PV$$

$$H^0 + H^{id} = E^0 + E^{id} + (PV)^0 + (PV)^{id}$$

(4.1)

where the superscript id refers to the ideal gas, $(PV)^{id} = RT$ and $(PV)^0 = PV - RT$. Thus

$$E^0 = H^0 - (PV - RT)$$

$$(E^0/RT_c) = (H^0/RT_c) - T^* (PV/RT - 1)$$

(4.2)

Eq. (4.2) was used to compute E^0/RT_c from the tables of Hougen and Watson for the lower values of T^* of interest. For $V^* = 0.80$ these are

T^*	H^0/RT_c	$T^*(PV/RT-1)$	E^0/RT_c
1.10	-3.00	-0.66	-2.35
1.23	-2.75	-0.42	-2.3
1.50	-2.25	-0.20	-2.05
1.76	-1.85	-0.04	-1.8

For higher values of T^* we refer to the values of A and N_2 given in Hirschfelder, et al³ p. 308. For A at $V^* = 0.77$, we have

$T^* = 1.69$	$E^0/RT_c = -2.00$
2.08	-1.87
2.62	-1.80

which can be made to join fairly smoothly to the data at lower T^* . In support of all these data, is the cell model calculation (which usually gives reliable energies) presented in ref. 3, p. 300 which for $V^* = 0.8$ gives

$T^* = 1.10$	$E^0/RT_c = -2.25$
1.23	-2.22
1.50	-2.15
1.76	-2.00

We shall, therefore, adopt the values of E^0/RT_c given in Table II, together with values for $V^* = 0.6$ for which the calculation follows the same pattern

TABLE II

E^0/RT_c as a Function of T^*

<u>(a) $V^* = 0.80$</u>								
$T^* = 1$	1.10	1.23	1.50	1.76	2.3	2.9	3.4	
$-E^0/RT_c = 2.5$	2.4	2.3	2.1	1.9	1.8	1.75	1.7	
<u>(b) $V^* = 0.60$</u>								
$T^* = 1$	1.05	1.11	1.21	1.33	1.6	1.9	2.4	
$-E^0/RT_c = 3.2$	3.15	3.1	3.0	2.9	2.7	2.5	2.3	

5. Calculation of Excess Entropy

The excess entropy can be calculated from the compilation of Hougen and Watson for the lower T^* . At higher values of T^* one may integrate using

$$(dS^e/dT) = (1/T) (dE^e/dT) \quad (5.1)$$

or compare directly with data of argon and nitrogen at high T^* . In order to have a consistent set of values, S^e should be adjusted so that Eq. (5.1) is true.

In using the graph of Hougen and Watson, care must be taken. Shown on the graph is $S - S_0(T) = R \ln p(V,T)$ where $p(V,T)$ is the real pressure of the gas at V,T . This is not the same S^e that is used in (5.1) which is $S^e = S - S_0(T) + R \ln P_{ideal}$. Thus

$$S^e = S_{H\&W}^e + R \ln(P_{ideal}/P) = S_{H\&W}^e - R \ln(PV/RT) \quad (5.2)$$

Eq. (5.2) may be used to convert the values of Hougen and Watson to S^e . For $V^* = 0.8$, the calculation is

T^*	1.10	1.23	1.50	1.76
S^e/R (H&W)	-2.3	-1.75	-1.2	-0.85
$\ln(PV/RT)$	-.91	-.53	-.22	-.04
S^e/R	-1.4	-1.2	-1.0	-0.8

These values are roughly consistent with the values of E^e/RT given in Table IIa. For argon at $T^* = 1.69$, $-S^e/R = 0.9$ (ref. 3, p. 310) a value which is consistent with the above. We shall adopt the above values with small modification to force agreement with (5.1). At higher values of T^* we shall adopt values through integration of (5.1). This leads to the values in Table III.

TABLE III

S^e/R as a function of T^*

(a) $V^* = 0.80$

$T^* = 1.10$	1.23	1.50	1.76	2.3	2.9	3.4
$-S^e/R = 1.3$	1.2	1.0	0.9	0.85	0.8	0.8

(b) $V^* = 0.60$

$T^* = 1.05$	1.11	1.21	1.33	1.6	1.9	2.4
$-S^e/R = 1.8$	1.7	1.6	1.5	1.3	1.2	1.1

6. Calculation of Adiabatic Work to Low Pressure States

We are now in a position to calculate the work that the system can do by adiabatic expansion from the high pressure states previously considered. We shall make the calculation for final states at 1,000 atm. ($P^* = .116$) 100 atm ($P^* = .0116$) and selected values at 1 atm.

In all cases, condensation occurs, so that one must calculate first the fraction condensed, say x . We present here a sample set of calculations beginning with $V^* = 0.80$ and expanding to a final pressure of 1,000 atm. To find the final temperature we assume that the data of Rau and Thorn¹ still apply. (Such extrapolations of vapor pressure data are usually valid, cf. Guggenheim² p. 141.)

$$T^* = \frac{23,330}{14,000} \frac{1}{8.58 - \log_{10} P_{mm}} = \frac{1.67}{8.58 - 5 - \log_{10} 7.6} = 0.617 \quad (6.1)$$

At such reduced temperatures the vapor may be considered ideal since the molar volume of the vapor is $\sim (RT/P) = (T^*/P^*) (V_c/0.3) = 16 V_c$.

To find x , one uses the condition that the change in entropy is zero. Thus

$$\Delta S = S_{\text{initial}} - S_{\text{final}} = (\Delta S)_{\text{ideal}} + S^{\circ} + x(\Delta H/T_{\text{final}}) = 0 \quad (6.2)$$

where S° is the excess entropy in the initial state and ΔH is the heat of vaporization at T_{final} . For lack of a better number, we shall keep $\Delta H = 3.8 RT_c$ for all temperatures. This may be rationalized by saying that the increase in $(PV)_{\text{vapor}}$ is offset by the decrease in ΔE in going from $T^* \approx 0.1$ to $T^* \approx 0.6$. Alternatively the assumption corresponds to $\Delta C_p \approx 0$ which is reasonable since for most liquids $C_p \approx (5/2)R$ in this region of temperature.

Again, care must be taken with $(\Delta S)_{\text{ideal}} + S^{\circ}$. We have

$$(\Delta S)_{\text{ideal}} = C_v \ln(T_2/T_1) + R \ln(V_2/V_1) = C_p \ln(T_2/T_1) - R \ln(P_2/P_1) + R \ln(P_2 V_2 / RT_2) \quad (6.3)$$

assuming $(P_1 V_1 / RT_1) = 1$. Thus the S° which enters into (6.1) is always in the combination $S^{\circ} + R \ln(P_2 V_2 / RT_2)$ which are the values directly tabulated by Hougen and Watson. However, for reasons of consistency discussed in Section 5, we shall use the values of S° presented there.

Solving (6.2) for x and using (6.3) we have

$$x = (-T_1^*/3.8) \frac{5}{2} \ln(T_2^*/T_1^*) - \ln(P_2^*/P_1^*) + \ln(P_2 V_2 / RT_2) + S^{\circ}/R \quad (6.4)$$

for which $T_1^* = 0.616$, $P_1^* = 0.116$, becomes

$$x = -0.373 \left[2.5 \log T_2^* - \log P_2^* + (S^0/2.30 R) + \log (P_2 V_2 / RT_2) - 0.409 \right]$$

Calculation leads to:

TABLE IV

Calculation of Mole Fraction of Condensate from
 $V^* = 0.8$ to $p = 1,000$ atm

T_2^*	$2.5 \log T_2^*$	$\log P_2^*$	$S^0/2.30 R$	$\log(P_2 V_2 / RT_2)$	Expression	x
1.10	.103	+0.267	-.618	-.380	1.570	0.59
1.23	.225	.477	.522	-.288	1.411	0.53
1.50	.440	.698	.436	-.096	1.199	0.45
1.76	.615	.846	.370	-.017	1.027	0.39
2.3	.905	1.000	.348	+.018	0.834	0.31
2.9	1.152	1.176	.348	+.094	0.685	0.26
3.4	1.329	1.300	.348	+.150	0.607	0.23

Similar calculations based on (6.4) lead to Table V.

TABLE V

Mole Fraction of Condensate

(a) From $V^* = 0.8$ to $p = 100$ atm.

T^*	1.10	1.23	1.50	1.76	2.3	2.9	3.4
x	.60	.56	.50	.46	.40	.36	.34

(b) From $V^* = 0.8$ to $p = 1$ atm.

T^*	1.10	1.76	3.4
x	.62	.50	.41

(c) From $V^* = 0.6$ to $p = 1,000$ atm

T^*	1.05	1.11	1.21	1.33	1.6	1.9	2.5
x	.72	.69	.67	.65	.60	.55	.47

(d) From $V^* = 0.6$ to $p = 100$ atm

T^*	1.05	1.11	1.21	1.33	1.6	1.9	2.5
x	.67	.65	.64	.62	.58	.55	.49

(e) From $V^* = 0.6$ to $p = 1$ atm

T^*	1.05	1.33	2.5
x	.68	.64	.54

Knowing x one may now compute the adiabatic work done since and we have all the necessary information to compute ΔE .

$$\int_{V_2}^{V_1} PdV = \Delta E$$

$$\Delta E = (3/2)RT^* + E^0 + x E_{\text{vap}}$$

or

$$\Delta E/RT_c = (3/2)AT^* + (E^0/RT_c) + x (E_{\text{vap}}/RT_c)$$

(6.5)

where E^0 is negative and is the cohesive energy of the initial state as tabulated in Section 4. For E_{vap}/RT_c , we shall assume the value 3.3 since we have assumed $(\Delta H)_{\text{vap}} = 3.8 RT_c$ at $T^* = 0.6$. We again present one sample calculation and the results of the remaining calculations.

TABLE VI

Adiabatic Work in Expansion from
 $V^* = 0.8$ to $P = 1,000$ atm

T^*	$3/2 T^*$	$x3.3$	$-E^0/RT_c$	Work/ RT_c
1.10	0.72	1.95	2.4	0.3
1.23	0.92	1.75	2.3	0.4
1.50	1.32	1.48	2.0	0.8
1.76	1.71	1.29	1.85	1.15
2.3	2.6	1.02	1.8	1.8
2.9	3.5	0.86	1.75	2.6
3.4	4.2	0.76	1.7	3.3

Similar calculations based on (6.5) lead to Table VII.

TABLE VII

Adiabatic Work in Expansion

(a) From $V^* = 0.8$ to $p = 100$ atm

T^*	1.10	1.23	1.50	1.76	2.3	2.9	3.4
Work/ RT_c	0.7	0.8	1.3	1.8	2.5	3.2	4.0

(b) From $V^* = 0.8$ to $p = 1$ atm

T^*	1.10	1.76	3.4
Work/ RT_c	1.0	2.1	4.3

(c) From $V^* = 0.6$ to $p = 1,000$ atm

T^*	1.05	1.11	1.21	1.33	1.6	1.9	2.4
Work/ RT_c	-0.1	0.0	0.1	0.3	0.9	1.3	2.1

(d) From $V^* = 0.6$ to $p = 100$ atm

T^*	1.05	1.11	1.21	1.33	1.6	1.9	2.4
Work/ RT_c	0.0	0.2	0.4	0.6	1.1	1.6	2.4

(e) From $V^* = 0.6$ to $p = 1$ atm

T^*	1.05	1.33	2.4
Work/ RT_c	0.4	0.9	2.7

We now summarize all interesting estimates separately for $V^* = 0.80$ and $V^* = 0.60$. Tables VIII and IX should be used in conjunction with the critical constants $T_c = 14,000^\circ$, $V_c = 40 \text{ cm}^3$, $P_c = 8,650 \text{ atm}$. The unit of energy is $RT_c = 28 \text{ kcal/mole}$. The unit of entropy is $R = 2.0 \text{ cal/mole}$. We shall call W_{1000} the adiabatic work done from a given initial state to $P = 1,000 \text{ atm}$ and similarly for W_{100} and W_1 . E is the energy required to reach a state from the melting point.

TABLE VIII

Summary Table for $V^* = 0.8$

T^*	P^*	PV/RT	$-E^*/RT_c$	E/RT_c	$-S^*/R$	W_{1000}/RT_c	W_{100}/RT_c	W_1/RT_c
0.99		~ 0.3	2.5	2.7				
1.10	1.85	0.40	2.4	2.95	1.3	0.3	0.7	1.0
1.23	3.0	0.59	2.3	3.25	1.2	0.4	0.8	
1.50	5.0	0.80	2.1	3.95	1.0	0.8	1.3	
1.76	7.0	0.96	1.9	4.5	0.9	1.15	1.8	2.1
2.3	10.0	1.04	1.8	5.35	0.85	1.8	2.5	
2.9	15.0	1.24	1.75	6.3	0.8	2.6	3.2	
3.4	20.0	1.41	1.7	7.7	0.8	3.3	4.0	4.3

TABLE IX

Summary Table for $V^* = 0.6$

T^*	P^*	PV/RT	$-E^*/RT_c$	E/RT_c	$-S^*/R$	W_{1000}/RT_c	W_{100}/RT_c	W_1/RT_c
0.96			3.2	2.0				
1.05	2.0	.35	3.15	2.1	1.8	-0.1	0.0	0.4
1.11	3.0	.48	3.1	2.2	1.7	0.0	0.2	
1.21	5.0	.75	3.0	2.5	1.6	0.1	0.4	
1.33	7.0	.95	2.9	2.8	1.5	0.3	0.6	0.9
1.6	10.0	1.12	2.7	3.4	1.3	0.9	1.1	
1.9	15.0	1.42	2.5	4.0	1.2	1.3	1.6	
2.4	20.0	1.50	2.3	5.0	1.1	2.1	2.4	2.7

7. Heat Capacity Considerations

Some interesting correlations of data on heat capacities in liquids have been pointed out by Bauer, Magat and Surdin⁷. For the three monatomic liquids A, Ne and Hg, all points fall on a "universal" curve if the temperature is parametrized as follows

$$\Theta = \frac{T - T_m}{T_c - T_m} = \frac{T^* - T_m^*}{1 - T_m^*}$$

where T_m is the melting point and T_c the critical point. Also we define $C_v^* = C_v - C_{v,ideal} = C_v - (3/2)R$. Then it is found that $C_v^* = 1.8R$ for $\Theta = 0$. This decreases rapidly to $C_v^* = 1.2R$ at $\Theta = 0.1$. It then levels off up to $\Theta = 0.35$ at the value $1.2R$ and finally slowly decreases to $0.5R$ at $\Theta = 1$.

The initial high value of $1.8R$ at $\Theta = 0$ is not surprising and is probably interpreted as a breaking up of local order just above the melting point. Such an effect may well vary from substance to substance. For U it has been found that $C_v^* = 3R$ just above the melting point. As no experiments have been carried out at higher temperatures, one is forced to conjecture that this is probably due to a residual breaking up of local order. In all probability over most of the liquid range C_v^* will behave as sketched above. The abnormally high C_v^* at T_m may be associated with the very low value of $T_m/T_c = 0.1$ where for most liquids it is 0.4 or 0.5 .

We may use the heat capacity data listed above to estimate the change in excess energy. To heat the liquid at constant volume from $T = T_m$ to $T = T_c$ removes an amount of excess energy equal to $0.9 RT_c$ according to the above data. If the liquid is now expanded from $V^* = 0.38$ to $V^* = 0.80$ we lose a little more energy. This is roughly consistent with our estimate of a loss of $(3.8 - 2.5) = 1.3 RT_c$. For $V^* = 0.60$, we have estimated the loss as $0.6 RT_c$ which is considerably less than what we would expect from the C_v data (here we would expect $\sim 1 RT_c$). This discrepancy becomes somewhat ironed out in the gas phase, but still leaves a discrepancy of a few tenths of RT_c in our quoted values. As the total energy to get to $T^* = 1.5$ is about $3 RT_c$, the discrepancy in total energy is of the order of 10% . We are inclined to believe the values quoted by us as obtained from the table of Hougen and Watson and corroborated by cell model calculations rather than those based on the heat capacity data which are a sampling of three substances, two of which are most unlike uranium.

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